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ORIGINAL ARTICLE

Bioadsorption of Methyl Orange Dye Using Egg Shells powder from aqueous solution

Mekdes Gerawork Kassa
Department of Chemistry, College of Natural and Computational Science, Debre Berhan University, Debre Berhan, Ethiopia
*Corresponding Author:
Email address: mgerawork2009@gmail.com

ABSTRACT
The principal objective of this study was to explore the feasibility of egg shell bioadsorbent to remove methyl orange dye from aqueous solution. The effect of contact time, adsorbent dosage, agitation speed and pH were investigated for this adsorption experiment. The crystallinity and different functional groups were analyzed using XRD and FTIR spectrophotometers respectively. Also the removal efficiency of the adsorbent was determined by using UV - Vis spectrophotometer. As the XRD results shows, the adsorbent was highly crystalline and from FTIR data all desired functional groups were observed which confirms the purity of the eggshell powder sample. Indeed, the maximum adsorption capacity (95.41%) of the egg shell was found at optimum pH 5, 20min contact time, 160 rpm agitation speed and 3gm adsorbent dosage. From this study the adsorption efficiency of the eggshell was highly dependent on pH of solution, adsorbent dosage, contact time and agitation speed. In general, egg shells have promising potential for the removal of organic toxic dyes such as methyl orange from aqueous solution so as to clean up the environment.
Key words: *Adsorption, Organic dyes, pH, Pollution, Waste water*

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INTRODUCTION

Back ground of the study

Organic dyes are major pollutants and has become of paramount concern to the environmentalists [1]. This is due to these organic substances have the potential to contaminate both ground and surface waters [2]. These water sources might be contaminated through run-off from agricultural land as well as from industrial wastes discharge has been of health effect to living organisms [3]. However, these organic dyes are commonly used in many industries broadly used in textile industries, they leads to pollution of water when they are discharged from these industries without proper treatment [4].

The most important dye is Methyl orange (MO), an anionic monoazo dye in textiles industries and other commercial products [5]. It is difficult to remove this dye from waste water due to its characters such as non biodegradability, having complex structure, stability to light, heat and oxidizing agents [6, 13]. A number of methods can be used to remove this dye from waste water; oxidation, ozonation, coagulation and flocculation, filtration, electrolytic as well as adsorption on activated carbon [7]. But because of having drawbacks such as the incomplete removal, low selectivity, expensive reagent and chemical use, high energy requirements and generation of toxic wastes other treatment methods have been discovered [8].

But adsorption is very cheap and effective compared to other methods. However, efforts have been contributed to develop new adsorbents and improving the existing adsorbents to have alternative materials to activated carbon [9]. Recently adsorption by using powder eggshells is becoming the much preferred method because of its low cost, simplicity of design, versatility, effectiveness, ease of operation and insensitivity to such toxic substances [6].

Therefore the principal objective of this study was to investigate the use of powdered eggshells bioadsorbents for the removal of MO dye from aqueous solution. Parameters such as adsorbent dosage, contact time, agitation speed and pH were investigated to test their effects on batch adsorption experiment. Also the structural properties, presence of different functional groups and the removal

efficiency of the as prepared bioadsorbent has been characterized by using XRD, FTIR and UV-Vis spectroscopic methods.

MATERIAL AND METHODS

Experimental sites

The materials used for this research was collected from different hotels and cafeterias of Debre-Berhan town which is located in northern part of Ethiopia, Amhara region 130km far from Addis Ababa, capital city of Ethiopia, And also the preparation of bioadsorbent and the adsorption experiments were conducted in chemistry laboratory, DebreBerhan University, Debre Berhan, Ethiopia. The properties of the bioadsorbent as XRD, FTIR spectroscopic techniques were characterized at Adama science and Technology University (ASTU), Adama and Addis Ababa University, Chemistry department.

Chemicals, Reagents and Apparatuses

The materials employed in this work include, electronics weighing balance, beaker (100mL), Magnetic stirrer, Measuring cylinder (100mL), conical flask, Test tubes, Centrifuge (800D), oven, sieve. And all chemicals and reagents used were of analytical graded namely, Sodium bi carbonate ($NaHCO_3$), Sulfuric acid (H_2SO_4), Distilled water, NaOH, Methyl orange dye(327.33g/mol) and egg shells.

Characterization

The structures of the as-synthesized bioadsorent was examined by Powder X-ray diffraction (XRD) using X´Pert Pro PANalytical equipped with an X-ray source of a CuKα radiation (wave length of 0.15406 nm) at step scan rate of 0.02^o (step time: 1s; 2θ range: 5.0^o - 90.4^o). The structural component was determined by FTIR (Shimadzu 8400). The degradation efficiency of the bioadsorbent was determined using UV-Vis absorption spectrophotometer (Shimadzu SP65).

Sample Preparation

Preparation of the adsorbent

The eggshell used in the experiment were collected from different hotels and cafeterias located in Debre-Berhan, Ethiopia using plastic bags and washed with tape water to remove surface adsorption then dried at 120°C for 2 h in a convection oven, grounded using mortar and pestle then socked with H_2SO_4 solution 1:1 ratio weight per volume for overnight to increase adsorption efficiency. Then washed with distilled water till it attained neutral pH and treated with 2%$NaHCO_3$ overnight in order to remove excess of acid present then it was washed with distilled water to remove dirt and boiled to remove color and dried in oven at 120^oC for 2 h and activated in muffle furnace at 450^oC for an 1 hours. Finally the dried calcined eggshell powder is allowed to pass through 2 mm sieves for the study [10, 11, 12 14, and 6].

Preparation of adsorbate solution

Methyl Orange (MO), a bright orange crystalline powder with a molecular formula of $C_{14}H_{14}N_3NaO_3S$, molecular weight of 327.33g/mol and maximum absorption (λmax, 465nm) used without further purification. A stock solution of methyl orange was prepared by dissolving 0.1g of the dye in 1L of distilled water and filtered via Whatman filter paper (No.1). The prepared stock solution was then wrapped with aluminum foil and stored in a dark to prevent exposure to direct light and the pH was adjusted by adding 0.1M NaOH solution and 1M HCl solution [13, 14 and 6].

Batch adsorption study

Batch adsorption studies for individual eggshell were carried out using 250 ml Erlenmeyer flask. The Dye concentration was estimated spectrophotometrically by monitoring the absorbance at 465nm using a UV-Vis spectrophotometer. The samples were withdrawn from the shaker at predetermined time intervals and the Dye solution was separated from the adsorbent by centrifugation at 4000rpm for 5min. The absorbance of Supernatant solution was measured by using Uv-Vis spectrophotometer. The effects of different parameters was carried out by varying adsorbent dose (0.5 – 1.5g), P^H of the solution (3-10), contact time (10-30min) agitation speed (100–160^oc) were used [15, 13]. Finally, the resulting suspension of the dye was filtered using a Whatman No.1 filter paper and the filtrate was analyzed by UV-Vis spectrophotometer to determine its adsorption efficiency. Removal efficiency was finally calculated by using the relationship [14];

$$\% \text{ Adsorption} = \frac{A_0 - A}{A} \times 100 \quad \ldots\ldots\ldots\ldots (1)$$

Where A_o = the initial absorption (mg/L) and A = final absorption (mg/L) of the dye being studied.

Effect of contact time

Contact time is one of the most important parameter for the assessment of practical application of sorption process of the determination of the rate of dye adsorption by the egg shell from 50ml of standard solutions; the quantity of dye adsorbed was determined by varying the contact time: 10, 20 and 30 min, when other parameters were kept constant.

Effect of adsorbent dosage

The effect of adsorbent dosage was studied by adding Samples of egg shell 0.5, 1.0, 1.5g to 50mL dyes solution in 250 ml Erlenmeyer flask and the adsorption efficiency for different dose was determined by keeping other parameters constant.

Effect of pH

To investigate the effect of initial pH on adsorption, the pH of the dye solutions was adjusted appropriately using 0.1M solutions of HCl and NaOH to range from (3–10). Exactly 50mL of dye was measured into each conical flask. 1.5g of the adsorbent was added and the flasks Stopper and shaken for 20 minutes using a laboratory shaker. The resulting suspension was filtered using Whatman number 1 filter paper and the filtrate analyzed using a UV - Vis spectrophotometer at the maximum wavelength of 465nm.

Effect of agitation Speed

The effect of agitation speed was conducted by varying speeds with 100, 120, 140 & 160 rpm, when other parameters kept as constant. So, by taking the optimum load of the adsorbent in 50mL of the dye solution the adsorption efficiency was measured for different agitation speed by UV-Vis spectrophotometer.

RESULT AND DISCUSSION

XRD analysis

X-ray diffraction pattern of the eggshell powder is shown in Fig. 1. XRD was used to investigate the diffraction pattern index and the crystal size of the adsorbent by assigning the correct Miller indices (hkl) to each reflection in the diffraction pattern. An XRD pattern is properly indexed when all of the peaks in the diffraction pattern are labeled and no expected peaks for the particular structure are missing. The results show the diffraction peaks obtained are characteristics of calcite ($CaCO_3$). Calcite is the thermodynamically most stable form of $CaCO_3$ at room temperature [16]. And this spectrum shows the phase structure of the powder eggshell was trigonal structure with crystal size of 52.97nm. Indeed, the peaks at 23(102), 29.36(104), 31.32(006), 35.94(210), 39.36(213), 43.14(202), 47.12(204), 47.48(108), 48.48(216) confirms the presence of Calcium Carbonate and the pattern obtained well matches with COD file No. 00-702-2027 [17]. Also at 25.51^0 $CaSO_4$ was observed, (COD file. 00-900-4096) [18], and at 34.17(101) $Ca(OH)_2$ was obtained (00-900-0113) [13].

The results revealed eggshells are mainly composed from $CaCO_3$ which shows its well crystalline structure enables for the best adsorption capacity of the adsorbent. Also less peaks of $Ca(OH)_2$ suggests the poor crystalline nature of the prepared sample in which similar reports has been reported by other researchers [14].

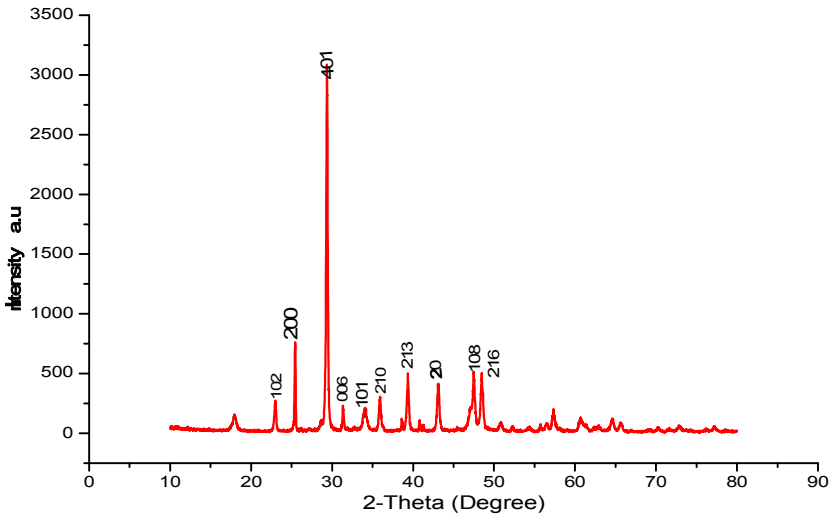

Figure 1: XRD spectrum of powder Eggshell

FTIR analysis

The presence of different functional group is shown in figure 2 and the spectrum is scanned from 4000 – 400cm^{-1}. The peak spectrums observed at 711, 871, 1798, 2513, 1413 and 1798cm^{-1} confirms the presence of $CaCO_3$. Also the peaks at 3336 and 3658cm^{-1} are because of N–H and C=O stretching bands in the eggshell powder [21]. The FTIR results show the prepared eggshell powder contains more peaks of $CaCO_3$ which confirms these bioadsorbents are highly composed from these carbonates and the purity of the sample which is in good agreement with XRD results.

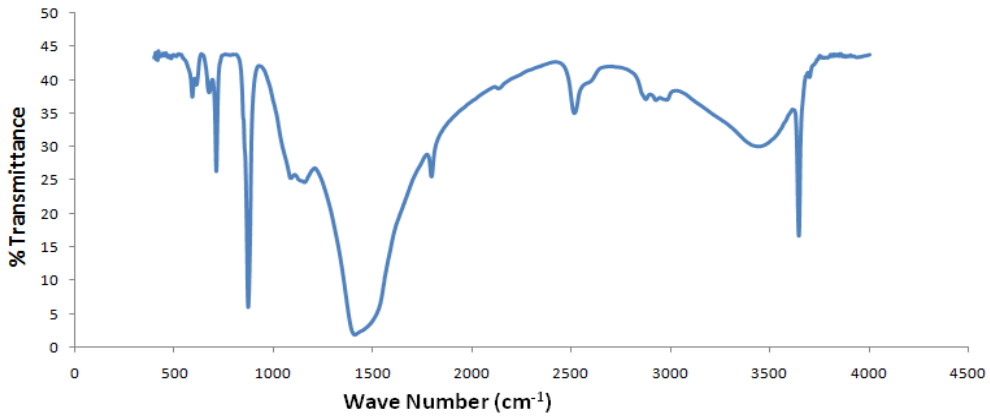

Figure 2: IR spectrum of the powdered eggshell

Batch adsorption experiments

The effect of various parameters namely, adsorbent dosage, pH of the solution and contact time on the adsorption capacity of egg shell in the removal of methyl orange dye from model dye waste water were discussed in the following sections.

Effect of adsorbent dosage

The effect of egg shell on the adsorption of methyl orange is shown in fig 3. From this as the amount of egg shell increases the removal efficiency also increases proportionately with some continuous variation. The optimum degradation efficiency was at 3g dosage with 90.1% of removal efficiency. This result confirm us the increase of dose of the adsorbent increases adsorbent sites. This is because of the increment of the surface area of the adsorbent and availability of more reaction sites which helps to a good contact with the desired dye. Therefore, the amount of dye uptakes increases and consequently leads to better adsorption efficiency and this result is in agreement with the study of [15].

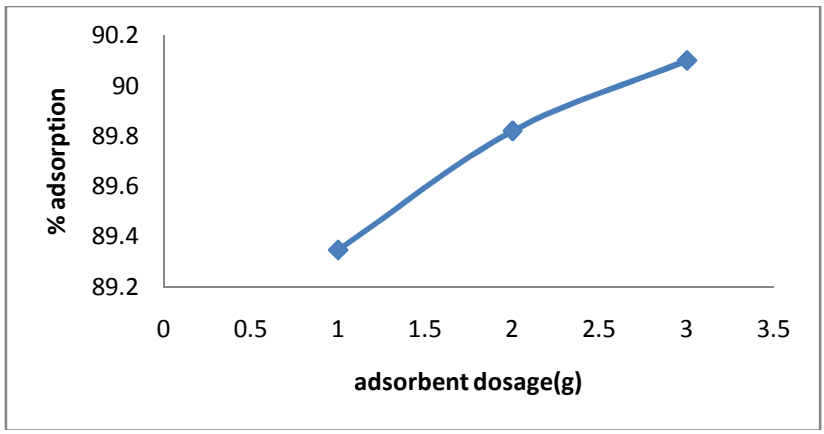

Figure 3: Effect of adsorbent dosage

Effect of contact time

Fig. 4 shows the effect of contact time on the adsorption of methyl orange. This was achieved by varying the contact time from 10min to 30min in separate experimental runs. The results revealed that the equilibrium adsorption rate was rapid during the first two 10 min and then becomes slower rate after 20 min. And the maximum adsorption efficiency of the adsorbent to decolorize the dye was 90.91%. This was due to the fact that, at the initial stage the number of free adsorption sites was higher and the slow adsorption rate in the later stage was due to slower diffusion of solute in to the interior of the adsorbent. The maximum adsorption occurred at 20 min and there was a slow decreament in adsorption efficiency

after this time because the equilibrium is attained. Different studies have reported the same impact of contact time on the removal efficiency of eggshells [18, 3].

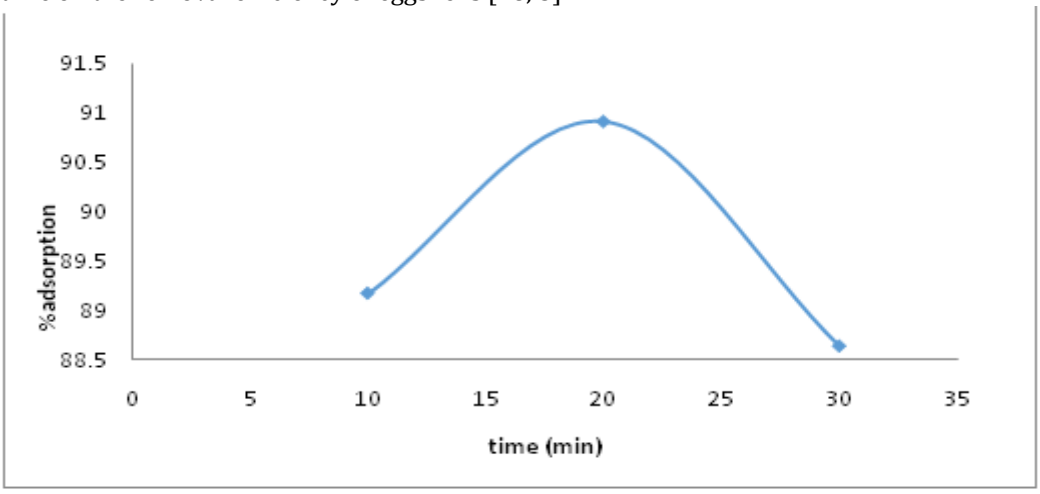

Figure 4: Effect of contact time

Effect of pH

The adsorption behavior of the targeted organic dye was highly affected by pH of the solution as shown in fig. 5 below. The percentage of the methyl orange removal was tested at 3, 5, 8 & 10 over other fixed operating conditions with decolorization efficiency of 95.21, 95.41, 92.3 and 89.25% respectively. It is seen that the percentage of dye removal was high at P^H of 5. Therefore, as well as providing more Ca^{2+} in solution from the dissolution of calcite, decreasing pH effectively increases the number of positive surface sites leading to an increase in the amount of methyl orange removed from the system. On the other hand, under highly acidic conditions, the decrease may be attributed to the combined effects of chemical and electrostatic interaction between the calcite surface and the methyl orange ions. In contrast, in alkaline solution the removal efficiency was decreased to 89.25%, it might be because of the repulsion between the adsorbent surface and the adsorbate [16,17]. From the result we can conclude that the adsorption efficiency of the eggshell was dependent on the pH of the solution [2].

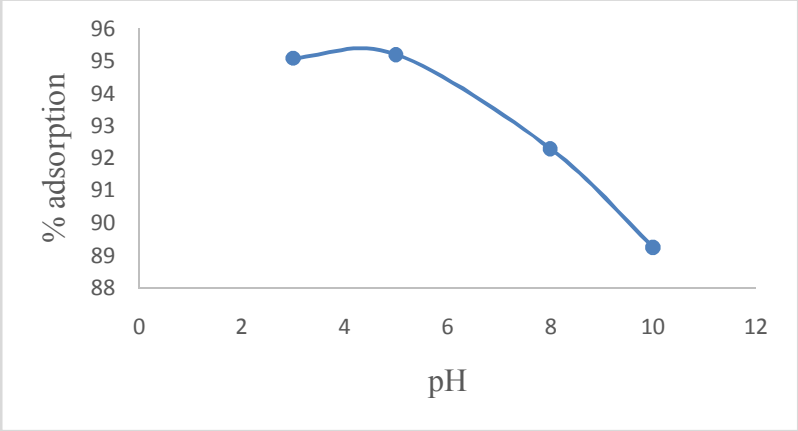

Figure 5: Effect of pH

Effect of agitation speed

The effect of agitation speed was conducted by varying speeds from 100, 120,140 & 160 rpm, when other parameters kept as constant. The influence of agitation speed on the extent of adsorption is shown in Figure 6 and the maximum degradation efficiency of the dye was 90%. At a given time, MO removal increases with the increase in the speed of agitation. The reason is that at higher speeds better contact between the adsorbent and adsorbate is possible. Similar findings for MO removal by using powdered eggshells have been reported by other investigator [19].

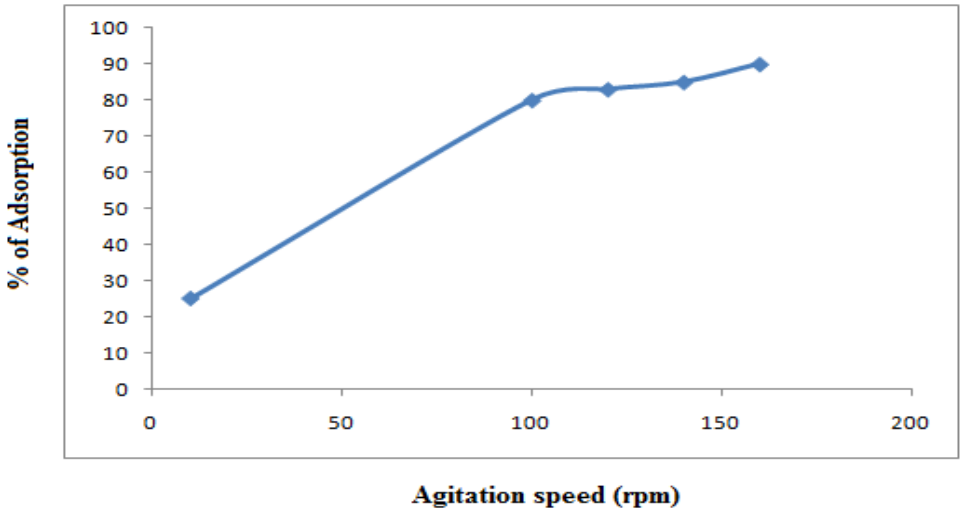

Figure 6: Effect of agitation speed

CONCLUSION

From this study eggshell powder is potential adsorbent for the adsorption of methyl orange dye with optimum degradation efficiency of 95.41%. The degradation efficiency of the adsorbent was prominently dependent with the operating parameters, adsorbent dosage, contact time, agitation speed and P^H of the solution. So, the optimal removal efficiency (95.41%) was at pH of 5, 3g of adsorbent dosage, 160 rpm of agitation speed and 20min of contact time. In conclusion, the results showed egg shell powder was proved to be a very effective adsorbent in the removal of methyl orange dye. Indeed, egg shells are dumped as a waste in a large amount and causes for the pollution of the environment. But in this study it is an effective biomass material that could be used as low cost adsorbent to remove such toxic organic dyes which couldn't be removed completely by using other methods because of their non-biodegradable nature from industrial waste water.

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